Nucleation in Supersaturated Objects

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(With 4 Figures in Text.)

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1 Theory

The path to be followed here goes back to considerations by W. Gibbs, which since then have been ignored when dealing with the question of nucleation[1], although it offers a way of dealing with the problem more precisely than has hitherto been done. For the sake of convenience, we shall first take a special case, namely the formation of the liquid phase from a supersaturated vapor of a pure substance (phase a). The pressure of the supersaturated vapor at the constant temperature T is p_r, while the lower pressure p_∞ means the pressure of the saturated vapor, i.e. the equilibrium pressure over a flat surface of the associated liquid phase (b). The vapor of pressure p_r is only stable under certain conditions, in particular only in the absence of the liquid phase. For this kind of conditional stability, the term metastability has been in use since Ostwald.

The reason for this type of stability has long been recognized in the capillary work involved in the formation of the new phase. As a proof for the correctness of this view one can use the calculations of Smoluchowsky[2]. If, as was done here, the capillary forces remain unconsidered, it follows that an appreciable quantity of substance can never be found in the supersaturated state for an observable time. The capillary forces are the sole cause of the metastability. It is therefore justified to use according to Gibbs as a measure of the (meta)stability of a supersaturated structure, e.g. steam, the work that has to be done against the capillary forces in order to create a state in which further Deposition of the new phase b takes place. It should be noted that the following considerations by Gibbs are strictly in the sense of classical thermodynamics, without considering fluctuations.

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[1] We would probably have missed the relevant chapters in the Thermodynamic Studies by W. Gibbs, 8. 296ff., if we had not made similar considerations before reading them.

[2] Ann. d. Physik **25**, 205 (1908).

To every pressure p_r there is assigned by the well-known equation by W. THOMSON

$$\mathscr{R}T \cdot \ln\left(\frac{p_r}{p_\infty}\right) = \frac{2\sigma \cdot M}{r \cdot d} \tag{1}$$

a spherical droplet of phase b (density d and surface tension σ) of radius r, which is right now in equilibrium with this pressure. Once a droplet of this characteristic size has been produced, an infinitely small amount of work suffices to make phase a completely unstable. The quantity sought after is therefore the work required to produce a characteristic droplet with surface area $\mathscr{F}$ inside a homogeneous supersaturated vapor which is as a measure of the stability of the supersaturated vapor of pressure p_r.

This work is, as GIBBS first derived using the thermodynamic functions, $W = \frac{1}{3}\sigma \cdot \mathscr{F}$, where $\mathscr{F} = 4\pi r^2$ a function of p_r according to Equation 1. In order to make it clear what amount of work is involved, the size is calculated in a clear way, in two different ways.

1. Way[3]. Inside a very large volume of supersaturated vapor of pressure p_r we think of a small closed cylinder with a piston containing some of phase b. The pressure that is exerted on the plunger and therefore prevails inside the phase b is p_r', in such a way that $p_r' - p_r$ is equal to the pressure that is only due to the capillary force which would prevail inside a characteristic droplet of radius r if one were present in phase a; This pressure is obviously

   $$p_r' - p_r = \frac{2\sigma}{r}\,.$$

   If now we replace the bottom of the cylinder with a wall that is only permeable to vapor, equilibrium prevails, since the phase b under the additional pressure $p_r' - p_r$ experiences an increases of the vapor pressure from p_∞ to p_r. At this pressure, we reversibly increase the volume of phase b by v by lifting the plunger, thereby gaining the work

   $$A_1 = (p_r' - p_r) \cdot v = \frac{2\sigma}{r} \cdot \frac{4}{3}\pi r^3\,.$$

   The corresponding amount of substance was taken from phase a, which is assumed to be comparatively large, such that the pressure has not decreased while the volume is kept constant.

   The semi-permeable bottom is now replaced by a wall with a small opening and the volume v of phase b is pressed out as a drop by applying suitable pressure to the plunger. The work to be done is

   $$A_2 = \int_0^r (p_r' - p_r)\,\mathrm{d}v = \int_0^r \frac{2\sigma}{r} \cdot 4\pi r^2\,\mathrm{d}r = 4\pi r^2 \sigma\,,$$

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[3] This subsequent process is already indicated by GIBBS.

the total work expended is then

$$W = A_2 - A_1 = 4\pi r^2\sigma - \frac{8}{3}\pi r^2\sigma = \frac{1}{3}\sigma \cdot \mathscr{F}\,.$$

2. Way. The difference of the free energy between a droplet of radius r and the same mass of homogeneous liquid is $4\pi r^2\sigma$.
   We create a droplet reversibly over the vapor state, starting from liquid en masse.

   a) Evaporation of the required amount of liquid at pressure p_∞ and pressure increase from p_∞ to p_r:

   $$-\frac{4\pi r^3 \cdot d}{3M} \cdot \mathscr{R}T + \frac{4\pi r^3 \cdot d}{3M} \cdot \mathscr{R}T \cdot \ln\left(\frac{p_r}{p_\infty}\right)\,.$$

   b) Generation of the droplet from the vapor

   $$W + \frac{4\pi r^3 \cdot d}{3M} \cdot \mathscr{R}T\,.$$

The sum of the work done is equal to the increase in free energy

$$4\pi r^2\sigma = W + \frac{4\pi r^3 \cdot d}{3M} \cdot \mathscr{R}T \cdot \ln\left(\frac{p_r}{p_\infty}\right)$$

and taking into account Equation 1

$$\begin{aligned} 4\pi r^2\sigma &= W + \frac{4\pi r^3 \cdot d}{3M} \cdot \frac{2\sigma \cdot M}{r \cdot d} \\ W &= \frac{1}{3}\sigma \cdot \mathscr{F}\,. \end{aligned}$$

Assuming that the homogeneous vapor mass is very large, the same amount of isothermal work is obtained even if the whole is in a heat-impermeable envelope. Then W is equally the total energy change of the system when producing the characteristic globule.
This quantity is introduced by Gibbs as a measure for the stability of the steam. A combination with Equation 1 results in

$$W = \frac{16}{3}\pi \cdot \frac{\sigma^3 M^2}{\mathscr{R}^2 T^2 d^2 \cdot \left[\ln\left(\frac{p_r}{p_\infty}\right)\right]^2}$$

for $p_r = p_\infty$ $W = \infty$ holds: Steam from pressure p_∞ is absolutely stable. As p_r increases, W decreases indefinitely, i.e. stability finally becomes 0.

If p_r is slightly larger than p_∞, one can substitute $\ln\left(\frac{p_r}{p_\infty}\right)$ for $\frac{p_r - p_\infty}{p_\infty}$; that is the relative supersaturation. If one calls W the "stability" of the phase, then one can say: *The stability is inversely proportional to the square of the supersaturation.*
A difficulty for the application of the equation arises as soon as p_r becomes so large that the associated r assumes molecular dimensions. One can then proceed with GIBBS in such a way that, instead of the real molecular aggregate, one imagines a homogeneous sphere whose radius r is so large that the vapor pressure is equal to that of the aggregate. It is quite possible to produce a homogeneous liquid with an arbitrarily high vapor pressure p_r by sufficient pressure. The radius r then has nothing to do with the actual dimensions of the molecular aggregate, e.g. it has to be set differently for the same number of molecules but different arrangement. In the quantitative treatment of this difficult area the topic of very high supersaturation will have to be excluded, where one gets up to the limit where $r = 0$ in the imaginary sphere, or $\sigma = 0$ in the real structure and thus $W = \frac{1}{3}\sigma \cdot \mathscr{F}$ and limit oneself to moderate supersaturation. In the former case, a supersaturated vapor is completely stable in the sense of the previous classic thermodynamic considerations, i.e. an external disruption of a work output of the amount W is required to disturb the stability.
To generalize the previous result, it should be noted that the value of $W = \frac{1}{3}\sigma \cdot \mathscr{F}$ is derived from $\sigma \cdot \mathscr{F} - (p'_r - p_r) \cdot v$, i.e. from the difference between the work required to form the surface of the droplet and the work done to create the volume. Such is the nature of the work that must be done in the formation of a new phase within a large system, regardless of whether it is a gaseous, liquid, or solid body. We want to use the name nucleus for the new phase of that size (and shape) which, corresponding to the characteristic droplet in the above special case, is in equilibrium with the supersaturated system. We can then briefly say: the work of nucleation measures the stability of a system in the supersaturated state with regard to the emergence of the relevant new phase. (This last addition is necessary when there is the possibility of formation of various new phases, such as in supercooled sulfur vapor at about 70 °C, where liquid monoclinic and rhombic sulfur can be formed.)
The nucleation work has been calculated by GIBBS for various other examples. For liquid or gaseous nuclei that are to be formed inside an infinitely large homogeneous phase, the work has the value $\frac{1}{3}\sigma \cdot \mathscr{F}$, where σ is now the general meaning of the interfacial tension, or what amounts to the same thing in this case, the specific free interfacial energy at the relevant phase boundary. For crystal nuclei it is $W = \frac{1}{3} \cdot \sum \sigma \cdot \mathscr{F}$ under the same conditions. (The term $\sum \sigma \cdot \mathscr{F}$ means: The specific interfacial energies at the crystallographically different boundary surfaces of the crystal against the homogeneous phase are to be multiplied by the relevant surface area and the sum is calculated from this). Of particular interest is the case where two phases a and b are already present and it is sought after the nucleation (phase c) at the boundary of these phases. In this case, too, the work is to be

calculated as the difference between the surface work performed and the volume work gained. For a lens-shaped liquid (or gaseous) nucleus at the boundary of two liquids it is determined according to

$$W = \frac{1}{3} \cdot (\sigma_{ac} \cdot \mathscr{F}_{ac} + \sigma_{bc} \cdot \mathscr{F}_{bc} - \sigma_{ab} \cdot \mathscr{F}_{ab}) \ .$$

The double indices denote the boundaries of the relevant phases. The work has a positive value as long as $\sigma_{ac} + \sigma_{bc} > \sigma_{ab}$, but in case of $\sigma_{ac} + \sigma_{bc} = \sigma_{ab}$, i.e. in the case where the lens, extended to a thin lamella, lies entirely between the two original phases, W equals zero. Incidentally, one can easily see from the following consideration that less work is required to form a lens-shaped nucleus from a phase boundary than to form a sphere inside the phase. If such a sphere transforms into the lens voluntarily when it comes into contact with the interface, i.e. with a decrease in free energy, then the work required for reversible generation is smaller by this amount of energy. The stability of a system that consists of two phases that are oversaturated with respect to one component[4], is zero if the interface of the two phases is completely wettable by the new liquid phase to be formed. Such an interface can therefore have a significant influence on the stability of the system. In the case just mentioned, it plays the same role that the presence of the new phase itself would play, i.e. the deposition of the substance with respect to which the system is supersaturated will take place immediately on it.

Nothing essential changes in the considerations if one phase is a solid body, only then a measurement of the σ values is not possible. However, a certain point of reference for relative considerations will then be provided by considering the contact angle. As is well known, if the solid interface is plane, the relation

$$\cos(\alpha) = \frac{\sigma_{ab} - \sigma_{ac}}{\sigma_{bc}} \ .$$

holds. This information also fails if crystal nucleation is envisaged instead of the liquid phase. For the time being, one can only carry out a calculation that is only valid for the absolute 0-point in special cases, otherwise one has to be content with a rough estimate of the size of W. If, e.g. the formation of crystal nuclei (c) on a surface of another crystal (b), which is very similar in structure to the one to be formed, is considered, one might expect that $\sigma_{ab} \sim \sigma_{ac}$ and σ_{bc} becomes small. In such cases, W can assume very small values, so crystal nucleation is almost as facilitated by the boundary as is liquid separation on wettable surfaces.

If we now want to know the actual behavior of a supersaturated system, the question arises: how does the nucleation work that determines our measure of stability relate to the frequency with which nucleation occurs voluntarily as a result of natural fluctuations[5].

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[4] It is of course irrelevant in which absolute quantity the component in question is present in the phases, nothing changes if it is practically only contained in the one phase.

[5] F. Haber, Ber. d. D. Chem, Ges. **55**, 1717 (1922).

In the following attempt to answer this question, we shall provisionally imagine a mechanism that prevents any nucleus that has formed from growing further. Then it will dissolve again after a more or less long duration of time. If one looks at the whole system over a period of time, there will be a nucleus present for a certain fraction of that time. If we call this fraction Z, the order of magnitude becomes $Z = e^{-\frac{W}{kT}}$[6]; because if we produce a nucleus by doing work W while simultaneously dissipating the same amount of heat W, the entropy has decreased by $\frac{W}{T}$, while the energy of the system has remained unchanged. With the assumed large expansion of the system, the temperature has remained constant despite the heat of condensation.

The probability that a nucleus prevented from further growth exists in the closed large system due to the voluntary fluctuations is expressed by the above equation. In the simplest way, one could further assume that the number of nuclei that grow to a visible structure per second, if this obstacle is not present, is proportional to the calculated stationary number of nuclei. This treatment would be entirely analogous to attributing the reaction rate to the heat of activation, which plays the same role as our W, according to ARRHENIUS[7]. This conclusion would be admissible if it could be shown that the number of permanently present nuclei is large compared to the number of particles growing per second.

In the case of droplet formation, for example, it would be better to proceed by first determining the number of nuclei that reach an area $f(r) \leftrightarrow f(r - \Delta r)$ every second, again assuming the obstacle. If τ is the mean dwell time in this area, and ϑ is the return time of the event mentioned, then $\frac{\tau}{\vartheta}$[8] is the probability for the existence of a nucleus of the specified size, namely

$$A \cdot e^{-\frac{W_r}{kT}} \cdot \Delta f(r)\,.$$

In the immediate vicinity of r the droplet is in almost indifferent equilibrium. The probability of mass gain and loss is equal; therefore the size of the droplet is only subject to fluctuations that follow GAUSS's error law. The time τ during which the size interval $\Delta f(r)$ is traversed on average can be specified under certain physical conditions. Then $\frac{1}{\vartheta}$ would be, which is the number of nuclei entering the size range every second, also known under the condition that the hindrance is present. One can now assume that when the obstacle is removed, the number of droplets formed every second is proportional to the number determined in this way. However, this number is modified by the very fact that outgrowth is taking place, and there always remains some uncertainty at this point. The path corresponds to one proposed in the field of reaction rates by G. A. CHRISTIANSEN and H. A. KRAMERS[9].

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[6] A. EINSTEIN, Ann. d. Physik **33**, 1275 (1910).

[7] Zeitschr. f. physik. Chemie **4**, 226 (1889).

[8] Vorträge über die kinetische Theorie der Materie und der Elektrizität. Contribution SMOLUCHOWSKI. Verlag Teubner, 1914.

[9] Zeitschr. f. physik, Chemie **104**, 465 (1924), footnote.

It is not the intention of the present work to carry out the theory to the greatest attainable accuracy, which would only be possible for a specific example. Rather, what follows is to show how a large group of phenomena, the connection between which is not clear at the moment, is governed by the same law. The examples will always deal with how, at a given supersaturation, nucleation is facilitated by certain circumstances. These are circumstances that reduce the work W to a fraction of its other value. Then it is mostly sufficient to know that the order of magnitude of the ratio of the nucleation rates is given by $e^{\frac{W_2-W_1}{kT}}$. Nucleation is only observable when W approaches the order of kT.

The case here is similar to that of increasing the reaction through a catalyst[10]. If, for example, there is a platinum catalyst in a mixture of oxyhydrogen, the reaction can only be observed here – according to Polanyi[11]– because the heat of activation is significantly reduced in this case. The homogeneous reaction does not appear and the exact ratio of the homogeneous and catalytic reaction rates is of no practical interest. The following numbers shown in Table 1 for water vapor at 300 °C abs. should give an idea of what values the exponent $\frac{W_r}{kT}$ takes.

$\frac{p_r}{p_\infty}$	1.001	1.015	1.11	2
r	1×10^{-4}	1×10^{-5}	1×10^{-6}	1.5×10^{-7}
$\frac{W_r}{kT}$	8.4×10^{7}	8.4×10^{5}	8.4×10^{3}	1.9×10^{2}
$\frac{p_r}{p_\infty}$	5	10	100	1000
r	6.5×10^{-8}	4.5×10^{-8}	2.3×10^{-8}	1.5×10^{-8}
$\frac{W_r}{kT}$	35	17	4.3	1.9

Table 1: Values of the exponent $e^{\frac{W_r}{kT}}$ for water vapor at 300 °C abs.

The enormous drop in the e power with increasing supersaturation is the reason for the observation of an apparent metastable limit. If there is an opportunity for nucleation in 10 % supersaturated water vapor at a point where the work W is significantly reduced, such as a wettable wall, then the probability with which the process occurs here is so much larger that it is only observed here.

The theory in its simple form cannot be applied to test series in which the growth rate of the nuclei plays a decisive role. In particular, one sees immediately that simply considering the quantity W, the number of nuclei in a melt must constantly increase with increasing supercooling. As is well known, according to TAMMANN's investigations, this increase in the rate of nucleation only takes place up to a maximum value, after which a steep drop occurs again. TAMMANN's nucleation numbers are obtained in such a way that the melts obtained for a certain time in a far supercooled state are first brought to a somewhat higher temperature in order to give the nuclei formed at lower temperatures the opportunity to develop. However, it should be noted that a nucleus that is stable at low temperatures is smaller than one at higher temperatures. If the growth rate of the nucleus is so low during the warming-up period that it does not reach the size required for the higher temperature, it melts again.

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[10] According to W. OSTWALD, the triggering processes in oversaturated structures form the 1st class of catalyses. Über Katalyse, Leipzig 1902.

[11] Zeitschr. f. Elektrochemie, **27**, 142 (1921).

These conditions will be dealt with in detail in connection with experiments on the dependency of the growth rate of crystals in melts on the true limit temperature, which have already essentially been completed.

2 Comparison with Experience

The following is an overview of the facts of experience in the field of nucleation from the standpoint of the foregoing theory. In the main, well-known facts are referred to, and only occasionally personal experiments[12] are mentioned, which proved to be necessary to fill in gaps.

2.1 Fluid Nuclei

There is a rich literature on the formation of droplets in water vapor. It appears that in none of the reported experiments was supersaturation driven to the point where nucleation in the homogeneous vapor was observed. In general, special experimental tricks are required to obtain supersaturated water vapor. If one tries to supersaturate saturated water vapor by simply cooling the storage vessel –roughly in the manner in which supersaturated salt solutions are prepared– the attempt fails. The water promptly condenses on the walls of the vessel. The reason is that water wets the usual vessel materials, e.g. glass, quartz. In this case, according to the above statements, $W = 0$, the separation takes place immediately when the saturation point is exceeded, just as if a water surface were present instead of the wettable wall. Any eventual supersaturation inside is thus eliminated as quickly as the molecules reach the wall. In order to produce supersaturated steam, mixtures of the steam with foreign gases, e.g. air, are used and the cooling is not achieved by heat extraction through the wall, but by adiabatic expansion. In this way, droplet formation has often been studied. R. v. HELMHOLTZ[13] reports that in air containing water vapor that had been filtered through cotton wool, at a ratio $\frac{p_r}{p'_\infty} = 10$ there was no trace of fog noticeable. On the other hand, fog formation was obtained even with comparatively low supersaturation if dust, ions or certain vapors were present.

The influence of dust particles has not yet been satisfactorily explained. The dust contained in the air consists of all the substances found on the earth's surface, e.g. quartz, clay, feldspat and other mineral substances, cellulose, living and dead albuminoids, etc. Almost all of these substances can be wetted by water. According to our theory, they behave towards supersaturated water vapor like water structures of the same size. Up to now, this has always been tacitly assumed when explaining the effect of dust. However, the justification for this is only proven by the explanations in the theoretical part. No such facilitation of nucleation in water vapor is to be expected from non-wettable dust, which consists e.g. of fat particles. The condensing effect of ions was already described by J. J. Thomson[14] attributed to the reduction of the surface tension by the electrostatic charge. In terms of our explanations, this reduces the size of W and the frequency of growing increases accordingly. This case will not be discussed in more detail here, as detailed processing will be communicated separately.

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[12] More details can be found in A. WEBER, Diss., Berlin 1924.

[13] Wied. Ann. **27**, 508 (1886).

The influence of such vapors on supersaturated water vapor, giving solutions of low vapor pressure with liquid water, ($p'_\infty < p_\infty$) is already always reflected in the increase of the ratio $\frac{p_r}{p'_\infty}$, i.e. to an increase in supersaturation. It is primarily about ammonia, sulfuric acid, nitric acid, hydrogen chloride and some others. The surface tension is only slightly changed by these electrolytes, on the other hand, according to Equation 1, the radius r of the nucleus becomes smaller, therefore W decreases. The theory dictates that vapors which greatly lower the surface tension of water without appreciably affecting the vapor pressure also strongly promote nucleation. Apparently this belongs to the one mentioned by F. Richards[15], but entirely unsatisfactory declared effect (by assuming a chemical process) of ether vapor on the steam jet.

In addition to ether, we allowed all kinds of substances to act on a sensitive jet of steam that are chemically indifferent to water but strongly reduce surface tension, such as chloroform, glacial acetic acid, acetone, and carbon disulphide, and we were able to demonstrate a strong formation of fog with all these substances, just as strong as that of the strongest ionization sources, e.g. peak discharge, glowing platinum wire. If the surface tension is reduced in the ratio $\frac{\sigma_1}{\sigma_0} = \frac{1}{\alpha}$, taking into account Equation 1, the ratios remaining the same, $W_1 = \frac{W}{\alpha^3}$. The nucleation work is thus considerably reduced by vapors that greatly reduce surface tension, and the number of nuclei is thereby significantly increased.

Other vapors that do not reduce either surface tension or vapor pressure, e.g. NH_3, have no effect.

Finally, for the sake of completeness, it should be remembered that all liquids near the critical point, where $\sigma = 0$, are not capable of supersaturation.

Liquid mercury does not wet glass walls. It is therefore possible to keep mercury vapor in a supersaturated state in glass vessels for a period of time without precipitation occurring. Gibbs already suggested the following attempt:

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[14] literature, see K. Przibram, Jahrb. Rad, u. Elektr. **8**, 285 (1911).

[15] Wied. Ann. **40**, 166 (1890).

"By experimenting with a liquid which does not wet the walls of the containing vessel, we can avoid the need to keep the vessel hotter than the vapor to avoid condensation. If a glass sphere with a sufficiently long tube is placed vertically in a mercury tank, the tube containing mercury and its vapor and the sphere only vapour, the height of the mercury in the tube offers a convenient and accurate means of measuring the vapor pressure. If the tube at the top of the column of liquid were heated above the temperature of the glass sphere, the latter would undergo compression as the liquid wetted the walls of the vessel. But since this is not the case, it is likely that, if the experiment is carried out with reasonable care, densification will not occur within certain temperature limits. Should liquefaction occur, it would be easy to notice, especially if the sphere was bent downwards, so that the condensed mercury would not run back into the tube. As long as no liquefaction occurs, it is easy to give arbitrary (different) temperatures to the sphere and the column of mercury in the tube. The temperature in the latter will determine the vapor pressure in the sphere. In this way it seems possible to obtain mercury vapor in the sphere of greater pressure than the pressure of the vapor saturated for that temperature."

We have done some experiments with supersaturated mercury vapor. Glass tubes in the form of Figure 1 were cleaned with boiling chromic sulfuric acid, rinsed with water, finally with conductivity standard, and heated in a hot air bath to about 350 °C while being heated for 6 to 8 hours and evacuated with a mercury vapor pump. Then some mercury was distilled into one leg and the tube was melted at the point indicated in Figure 1. The vacuum of the tube was subsequently checked again by alternating current discharge with external electrodes. To get rid of nuclei, the leg, in which the shoe was to appear later, was heated in a water bath to 100 °C for 1/2 hour. During the execution of the experiments, this leg was always kept at 0 °C in a thermos flask with melting ice. The temperature of the mass of liquid Hg in the second leg was variable at will in the individual experiments. If the warmer leg had a temperature of 2 °C, taking into account the flow resistance of the pipe into the colder leg, in 5 min 2×10^{-4} g Hg would have been over-distilled if the deposition had taken place without obstacles. In fact, no visible amount of mercury was present during this time, but the above weight amount was only deposited after 6 hours. After several hours of testing, the glass wall showed a mist of Hg droplets fairly evenly distributed over the entire surface of the cooled leg, proving that the formation had not occurred internally but on the wall itself. A series of experiments, which were supposed to show the dependency of the number of droplets on the supersaturation, led to the strange result that the number increased almost linearly with the pressure. This result is difficult to understand. We are forced to assume that the glass wall contains a small number of small spots of varying size which can be wetted by mercury and which, like the wettable dust particles in the case of water vapor, act like mercury nuclei of the same size. The nucleation on the actually pure glass surface is probably not observed in the tests, as originally expected. Therefore, tests with different types of glass (Thüringer, Jenaer Geräte and Duraxglas) did not lead to satisfactory results. The droplets are deposited on Durax glass with a different contact angle (135°) than on the other two types of glass, about 113°. In fact, under the same conditions, the number of nuclei on the former was lower, but not to the extent that might have been expected. For further comparison, test tubes were made which contained other substances in one leg, namely lead glass, beryl, orthoclase, galena, mica, platinum and gold. All showed larger droplet counts than the glass. In the case of platinum and galena, on which Hg does not yet completely melt, a temperature difference of 0.7 °C was sufficient to produce a dense fog in a short time. Gold fogged up even without a temperature difference. This metal behaves towards mercury vapor like a wettable and soluble salt towards water vapour. Even before saturation, the vapor separates to form a solution. The spot on the glass wall over which these materials had slid when the metals and galena were introduced in the glassware always showed the deposition of numerous droplets, proving that fine particles had been abraded.

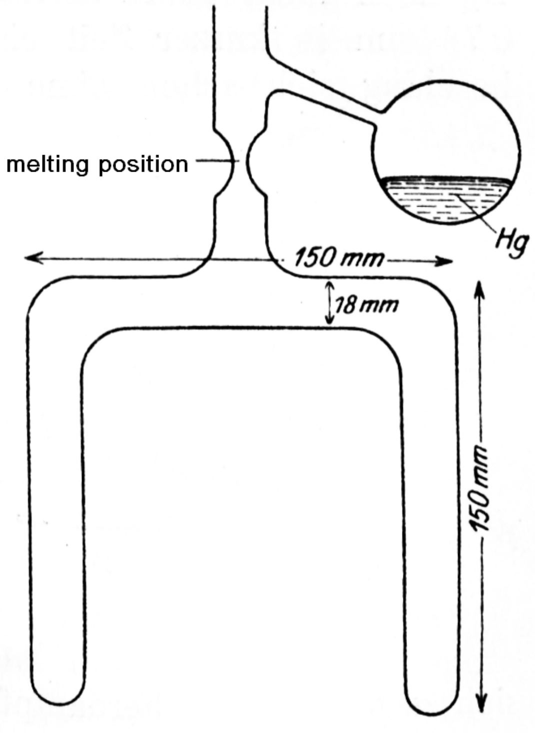

Figure 1: Experimental setup for experiments with supersaturated mercury vapor

The different effect of gold and platinum must of course also appear when mercury is separated from some other phase instead of the vapor, e.g. in electrolysis. A 1/20 norm. $HgNO_3$ solution served as the electrolyte. The large anode consisted of (liquid) Hg, the cathode in one case was made out of an Au wire, in the other case out of a Pt wire of the same size. Figure 2 shows the dependency of the current, i.e. the amount of mercury deposited every second, on the potential.

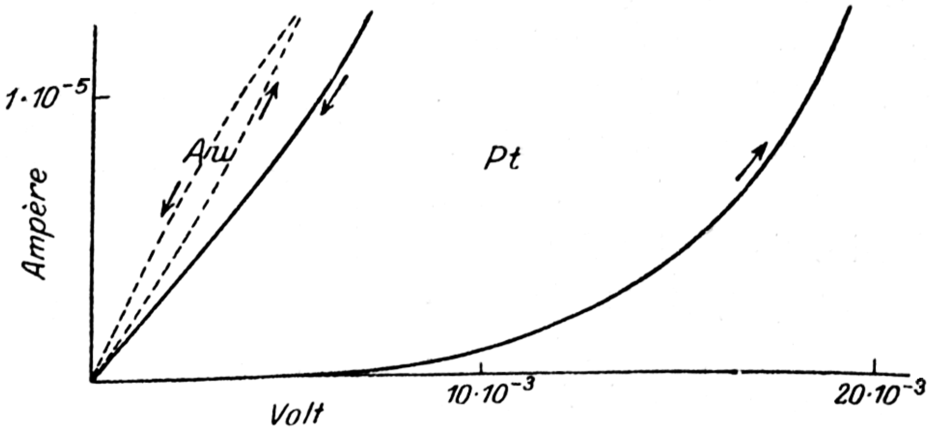

Figure 2: Current vs. potential of a galvanic cell consisting of an Au and Pt electrode in a 1/20 norm. $HgNO_3$ solution

In both cases, the electrodes were short-circuited for a long time, with the Au cathode already amalgamating.
Figure 2 now shows that noticeable Hg deposition only started at the Pt cathode at a voltage of 1 V to 2×10^{-3} V, while the mercury separated immediately at the gold cathode. The width of the loops, on the borders of which the points of a back and forth series of measurements lie, gives an approximate measure of the size of the metastable area in the case of the platinum electrode, while there is no such area in the case of gold. The slight difference in the backward and downward curves is probably due to differences in concentration.
The facilitation of nucleation through more or less wettable surfaces has gained a certain practical importance in the production of MOSER's breath images and above all in the daguerreotype, which forms the basics of photographic technology.

2.2 Crystal Nuclei

Nothing more is known about homogeneous crystal nucleation from the gaseous phase; it should not be excluded in the case of high supersaturation, as is the case when HCl and NH_3 come together at atmospheric pressure for the resulting ammonia. However, R. v. Helmholtz indicated that in dust-free air he did not observe any formation of fog here either. On the other hand, the formation of carbon particles in a luminous flame is certainly a homogeneous nucleation. In solutions, too, this is not as common as is commonly assumed. It only occurs with certainty at very high levels of supersaturation, as is the case when chemical reactions are used to produce practically insoluble compounds. So one can hardly doubt that in the precipitation of iron hydroxide, alumina, etc., the nucleation takes place homogeneously.

In contrast, the homogeneous nucleation in less supersaturated solutions is doubtful. During an investigation into the formation of the Liesegang rings[16] one came to the conviction that nucleation starts always at already existing particles. Technical experiences also seem to confirm this view, one need only recall the crystallization of candy on cotton threads, and the use of lead plates to separate various crystallized salts from their solutions. It seemed desirable to us to demonstrate the influence of solid materials on nucleation by means of experiments we carried out ourselves. In order to obtain solutions that are as free as possible of foreign particles, it turned out to be the most expedient to aspirate the diluted solution through an ultramembrane filter (according to Zsigmondy-Bachmann) with the water jet pump and to evaporate it on afterwards in flasks from Jenaer Glas up to the desired concentration. The precipitation and decantation method was also tried, but the first gave the best results.

After evaporating the solution – the Jena flasks had previously been boiled for hours with a mixture of potassium bichromate and sulfuric acid and then steamed – it was placed in the saturation flask, whose rubber stopper (see Figure 3) has three holes. The U-shaped blow-off tube runs through the first hole, the blow-in tube through the second and finally the guide for the glass stirrer goes through the third. The lower part of the inner leg of the blow-off pipe is closed off by a cemented, fine-pored porcelain filter plate, which is followed inward by a layer of glass wool stuffed tightly. The technique of saturation consisted in reaching the point of saturation from the area of supersaturation. This had the advantage that the disturbing dust particles that might have gotten in from the air due to the overfilling during the manipulations that had already been carried out were precipitated by adsorptive crystallization; this resulted in a further purification of the solution.

The saturation flask was placed in a thermostat with a capacity of about 150 liters, the temperature of which was kept constant at ±0.2 °C by a thermoregulator

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[16] Notboom, Kolloidzeitschr, **32**, 247 (1923).

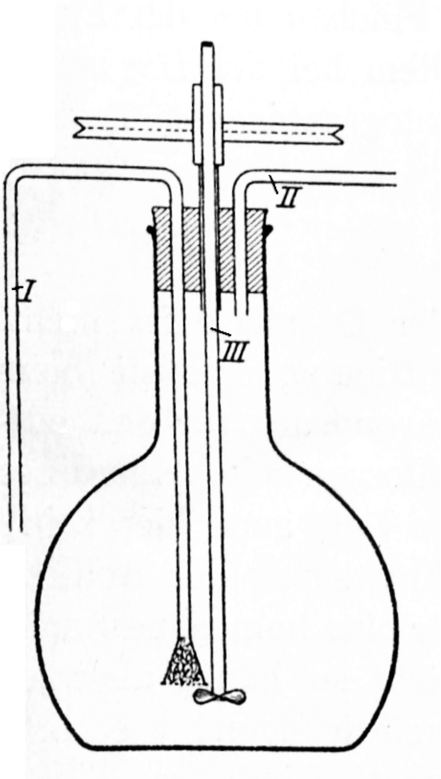

Figure 3: Experimental setup for homogeneous nucleation in supersaturated solutions

filled with toluene while stirring constantly. The stirrer in the saturation flask was turned at such a high speed that it constantly whirled the solid sediment through the solution.
The Erlenmeyer flasks used for the experiments were treated like the saturation flasks. The saturated solution was blown into them through the blow-off pipe from the saturation vessel, about $50\,\mathrm{cm}^3$ to $60\,\mathrm{cm}^3$ each. A cotton swab was used to seal the piston openings.
Before the solutions prepared in this way were placed into the thermostat, the freshly split crystal fragments of insoluble minerals were put into them and then heated once more to a temperature 30 °C higher than corresponds to saturation. The desired supersaturation was achieved by cooling inside the thermostat.
The experiments were carried out with solutions of the alkali metal halides NaCl, KCl and KBr. The results of the KBr solutions are compiled in Table 1.

Working with alkali metal halides has one major disadvantage. They are too easily subjected to external influences; their supersaturated solutions change their metastable state too quickly in air, which suggests that the dust flying around contains substances that have a specific nucleating effect for these salts.
Therefore, $NaNO_3$ and $K_2Cr_2O_7$ were used for the following experiments. The

Crystal	Lattice system	Cleavage plane	Temperature,°C	Supersaturation $\ln\left(\frac{c'}{c_\infty}\right)$
Baryte	orthorhombic	area of the base (001)	$28 - 24.2 = 3.8$	0.0473
Orthoclase	monoclinic	area of the base (001)	$28 - 23.9 = 4.1$	0.0509
Muscovite	monoclinic	area of the base (001)	$28 - 23.6 = 4.4$	0.0544
Selenite	monoclinic	2. pin. (010)	$28 - 23.3 = 4.7$	0.0579
Calcite	trigonal	rhombohedral face (100)	$28 - 21.2 = 6.8$	0.0856
Albite	triclinic	area of the base (001)	$28 - 21 = 7.0$	0.0877
Quartz	trigonal	imperfect according to the pyramidal surface (1011)	$28 - 20.8 = 7.2$	0.0906
Galena	cubic	cubic face (001)	$28 - 20.4 = 7.6$	0.0972
Potassium bromide	cubic			
		Reference solution:	$28 - 8 = 20$	0.2754

Table 2: Influence of solid materials on nucleation by supersaturation experiments using a KBr solution as an example

Crystal	Lattice system	Cleavage plane	Temperature,°C	Super-saturation $\ln\left(\frac{c'}{c_\infty}\right)$
Baryte	orthorhombic	area of the base (001)	80 – 67.5 = 12.5	0.1722
Orthoclase	monoclinic	area of the base (001)	80 – 65.9 = 14.1	0.1954
Muscovite	monoclinic	area of the base (001)	80 – 68.8 = 11.2	0.1520
Selenite	monoclinic	2. Pin. (010)	80 – 62.3 = 17.7	0.2505
Calcite	trigonal	rhombohedral face (100)	80 – 72.2 = 7.8	0.1030
Albite	triclinic	area of the base (001)	80 – 68.3 = 11.7	0.1575
Sodium nitrate	trigonal			
		Reference solution:	80 – 20 = 60	1.3654

Table 3: Influence of solid materials on nucleation by supersaturation experiments using a $NaNO_3$ solution as an example

Table 3 and Table 4 reflect the results.

The last two tables clearly show the influence of minerals on nucleation. The structural relationship of chile saltpeter to calcite means that the calcite–nitrate interfacial energy is small, while the corresponding interfacial energy against the solution will not be very different, so W is also only small.
Fluorspar has the same effect in a supersaturated KCl solution. In any case, after these experiments carried out, there can no longer be any doubt as to the specific influence that crystalline interfaces exert on nucleation.
The different effects of the different faces of a crystal are remarkable. Already in the first series of experiments, the observation was made that the first small crystals appear primarily at the edges of the cleavage planes. This phenomenon could be determined most clearly in fragments of heavy spar, mica and Selenite, but also in fluorspar and cryolite. In the experiments, the results of which are summarized in Table 2, the strong nucleating effect on the side surfaces of the baryte, gypsum and mica split pieces was particularly striking. The explanation probably lies in the fact that the interfacial energy is particularly high at these

Crystal	Lattice-system	Cleavage plane	Temperature,°C		Super-saturation $\ln\left(\frac{c'}{c_\infty}\right)$
Baryte	orthorhombic	area of the base (001)	$81-46.2$	$=34.8$	0.5642
Orthoclase	monoclinic	area of the base (001)	$81-67$	$=34$	0.5614
Muscovite	monoclinic	area of the base (001)	$81-48.7$	$=32.3$	0.5122
Selenite	monoclinic	2. Pin. (010)	$81-51$	$=30$	0.4652
Calcite	trigonal	rhombohedral face (100)	$81-44.7$	$=36.3$	0.5913
Albite	triclinic	area of the base (001)	$81-43$	$=38$	0.6356
Potassium dichromate	triclinic				
		Reference solution:	$81-34.7$	$=46.3$	0.8543

Table 4: Influence of solid materials on nucleation by supersaturation experiments using a $K_2Cr_2O_7$ solution as an example

points. This makes the subtrahend large in the expression for W.

This is where the following well-known experiment belongs: If one runs a needle over a mica sheet – even if only gently – so that a crack can hardly be seen with the naked eye, one can make it significantly visible by placing the mica sheet immediately in a supersaturated solution; the crystals of the dissolved salt, which form almost exclusively along the line, show the scratch very clearly. The rubbing of a vessel wall with a glass rod, which promotes crystal deposition, can undoubtedly be explained in a similar way.

Examples of how the different faces of the crystals affect nucleation to different degrees are known from mineralogy. The chlorite coatings of some alpine adularia, albites and rock crystals are limited to very specific surfaces. Finally, the fact is noteworthy that quartz in coarse pieces (quartzite) brought about crystallization much earlier than a homogeneous, broken quartz crystal. However, if one considers that there are many irregularly splintered small crystals next to one another on the fracture surface of the solid piece, then this appears to be quite understandable after the explanations given.

2.3 About directional Crystal Nucleation

At the boundary between two crystals, the interfacial free energy must be determined not only by the nature of the materials, but also by the mutual orientation. The extent to which the two lattices are twisted relative to one another also determines the size of the specific interfacial energy on the growth surface; preferred directions will be characterized by minimum specific interfacial energy. Our theory therefore leads us to expect that these directions of minimum specific interfacial energy will stand out due to their frequency when many crystals of the same substance grow on the crystalline substrate. When selecting the substances, however, the following must be observed:

In the case of two lattices that differ greatly in their structural elements, the inherently large distortion of the two crystal lattices that have grown together at the interface will cause the influence of orientation to recede. The minima will therefore be very flat in this case. For the size of the nucleation work, it is irrelevant in which position the nucleus comes to its crystal growth area.

If, on the other hand, the two lattices are very close to each other in terms of fine structure, then there will be strongly pronounced minima of the work W and the regular or symmetrical intergrowth will occur preferentially.

According to the procedure of F. Rinne, experiments were carried out in such a way that a drop of the salt solution saturated at room temperature was placed on the crystal growth surface and then a cover slip was placed over it. The evaporation of the water at the edges of the coverslip caused the supersaturation necessary for crystal formation.

When KCl crystals are deposited on a rock salt cube, most of them are arranged parallel to the edges of the cube, but a few are twisted relative to the base due to the lower probability of the process. Incidentally, the small crystals only adhere very loosely to the rock salt surface. This is easy to understand; because only if the common boundary surface is sufficiently small will the difference in the lattice spacing not cause any distortion; However, the growth in width of the nucleus in the growth with the substrate will be inhibited by the increase in the specific interfacial energy even after the accumulation of a few molecules. Once the nucleus has formed on a very small basis in this way, it continues to grow as if the rock salt base were not there at all, and its intergrowth with it may take place later in a few places.

In the same way KBr exhibits intergrowth together with rock salt; however, the number of twists has already increased noticeably. $NaNO_3$, which crystallizes trigonally in rhombohedra, grows parallel to a calcite rhombohedron.

Oriented tetrahedrons of KI are obtained on a mica base, which was already known to FRANKENHEIM[17]. According to GROTH[18] it crystallizes from aqueous solutions mainly in cubes or (more rarely) in octahedrons. In contrast, according to Figure 4, the tetrahedron nuclei are formed at the interface in one direction with just as little or even less work than the cube-shaped ones in any orientation.

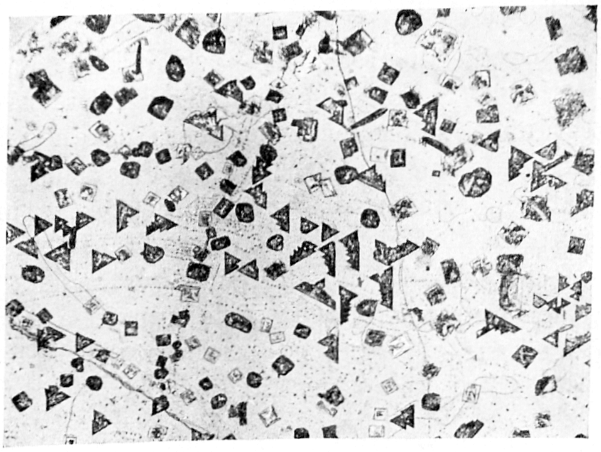

Figure 4: Crystallized KI on a mica base

On Selenite the crystals of the salts $CuSO_4 \cdot 5\ H_2O$, $Fe(NH_4)_2 \cdot (SO_4)_2$, $Na_2S_2O_3 \cdot 5\ H_2O$ show a directional arrangement.

KLOCKMANN[19] mentions that very often the vertical surfaces of the potassium feldspars are studded with albite crystals, so that the surfaces of both minerals that have grown together have the same indices and a common vertical axis.

When crystal nuclei and nucleating crystals come very close to each other in their structure, we are dealing with an isomorphic intergrowth. Because W is quite small here even at low supersaturation, the isomorphous salts in a supersaturated solution of their partner will be characterized by the fact that they cause the crystalline phase to separate very close to the saturation point.

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[17] cf. O. LEHMANN, *Molecular physics* 1888.

[18] cf. GROTH, *Elemente der physik. and chem. Kristallographie* (1920).

[19] *Lehrbuch der Mineralogie*, S. 137 (1922).

If the structural relationship is very high (e.g. for potassium and sodium alum), the probability of the formation of the new phase will be very high; in fact, a crystal of one continues to grow in the solution of the other just above the saturation point.

3 Nucleation on the Material itself

If one places a crystal of a substance into a gaseous or liquid phase, with respect to which the phase in question is supersaturated, the substance separates out on it. However, by no means does the crystal always continue to grow as a single crystal, but in general a disordered crystal aggregate is formed. The general feature of the phenomenon is as follows: if the supersaturation is low, a single crystal is formed; if it is larger, a structure appears which consists of a small number of larger individual individuals. If the supersaturation increases further, the number of crystal individuals increases and their size decreases. These facts are well known, they are described according to TAMMANN by introducing the concepts of crystal growth rate and nucleation rate. An explanation does not yet exist, it will be given in the following in consistent application of our theory.

The deposition of a crystalline phase differs, what already GIBBS[20] pointed out, basically from the deposition of a liquid phase. While a liquid phase is capable of absorbing every incident molecule, i.e. it can grow steadily, so to speak, crystal growth is impossible unless new lattice planes can be formed. The first creation of a new lattice plane presents a difficulty that is quite analogous to nucleation. Classically thermodynamically –and this is the position of GIBBS expressed in a different way of the statement on page 10– further growth of a crystal just beyond the saturation point is not possible at all, but a certain state of supersaturation is necessary in order to allow the creation of a new lattice plane at all. GIBBS must assume that different minimum supersaturation levels are required for crystallographically different surfaces. After that it should be possible to only grow surfaces of one kind close to the saturation point. Here our view differs from GIBBS's in that we conclude that there are only differences in the frequency of nucleation. The amount of work W required to create a new lattice plane is, already slightly above saturation, a small quantity caused only by the free energy of the edge forming the circumference of the lattice plane. At higher supersaturations, as soon as W is no longer large compared to kT, the e power alone is not decisive for the frequency of nucleation. Close to saturation, where the growth of a monocrystal can best be followed, it might be worthwhile according to one of us[21] to try, in modification of the older statements, to attribute the growth rates in different directions solely to the difference in the work carried out on the creation of new lattice planes.

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[20] Loc. cit., pp. 380-381, footnote.

[21] Volmer, Zeitschr. f. physik. Chemie **102**, 267 (1923).

In addition to the possibility of the formation of a crystallographically correctly oriented nucleus, there is always the possibility of the formation of an unoriented nucleus, just like on another substrate, but only because of the much greater work that is required for this – because a new interfacial energy occurs – the formation will be rarer. It will only become more frequent with higher supersaturation, namely when also the work W assumes small values for this type of nucleation. Then the factors in front of the e power will be decisive for the relative frequency of the two processes and it is clear that these shift the probability in favor of the formation of unoriented nuclei, since the possibilities for growth are much more numerous in this case. With increasing supersaturation, the formation of unoriented nuclei will thus continuously be favored. If one determines the average size of the individual individuals in such a crystal aggregate, then the number of their molecular layers directly indicates the ratio of the number of oriented nuclei to unoriented ones.

Between the formation of crystallographically completely oriented nuclei and those of disordered nuclei, regular intergrowth of the individual crystals can occur, as we see it in twinning, if certain directions with minimis of the interfacial energy are still present, to which then necessarily minima of W are assigned to.

In electrolytic crystal growth, the metallic deposit layer on a shellac-coated cathode often shows the structure of the parent sheet. This is not due to the fact that the directing force of the parent electrode crystals extends beyond the protective layer, but the interpretation is that small crystals can grow in the gaps and cracks in this protective layer towards the parent sheet, which then subsequently form above the layer through nucleation orientation to grow together according to the structure just mentioned.

Intergrowth often occurs with surfaces other than those that are crystallographically equivalent; e.g. in the case of the alkali halides, the rhombic dodecahedron face tends to grow together with the cube face of the newly formed crystal.

In most cases, even with very high supersaturation, ordered nucleation is more likely than completely disordered ones. Only rarely can levels of supersaturation be reached where the work W is of the order of kT and smaller for any type of nucleation. But then the size of the single crystal is shifted towards molecular dimensions, where the lack of a regular lattice formation becomes apparent in the disappearance of the DEBYE-SCHERRER diagram. HABER[22] obtained such precipitates through the rapid preparation of extremely poorly soluble precipitates by relatively concentrated reagents.

The formation of amorphous precipitates under such conditions results here as a conclusion from the general considerations given at the beginning. In our theory, it is not the rate of accumulation that is decisive, but the degree of supersaturation. It is not $c - c_\infty$ that appears, but $\frac{c}{c_\infty}$, a quantity that increases proportionally to the insolubility. This is introduced as the main point alone.

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[22] Ber. d. D. Chem. Ges. **6**, 1721 (1922).

The above considerations apply equally to crystal formation from vapours, solutions, melts and crystalline phases. The latter process is worth mentioning for its practical importance. The production of metal single crystals takes place after preparatory processes in that the crystallites of the metal piece are put in a position of a constrained state by suitable mechanical influences, which corresponds to an increased thermodynamic potential.

It is essential that this compulsion is extremely slight, just enough to make the tendency towards conversion noticeable. Only this state of slight supersaturation is capable of creating a monocrystal in the sense of the above explanations. If the constrains are higher, in addition to the strictly ordered nucleation, there is also unordered nucleation, which leads to the formation of a multi-crystal structure.

Experiments on the formation of metal deposits from supersaturated vapors[23] show that a supersaturated adsorption layer exists on the surface of growing crystals. If a solid layer of mercury is exposed to a stream of mercury vapor at about −60 °C, the density of which is large compared to the density of the saturated vapor at −60 °C, one finds that not all atoms be condensed, but that about 5 % return to the gaseous space. While one used to speak of reflection, more recent investigations[24] ensure that all molecules falling on solid bodies are first adsorbed. With substances that conduct heat well, the heat released is dissipated quickly enough for the temperature of the adsorption layer to be set equal to that of the crystal. If the adsorption layer were in thermodynamic equilibrium with the crystal, no more molecules could escape from it than would correspond to the maximum evaporation rate at the temperature in question. However, the fact that the number evaporating from the layer is actually greater proves that the adsorption layer is in a supersaturated state. (The higher “molecular reflection” in poor heat conductors is also due to the increased temperature of the boundary layer)[25]. The structure of the deposits of the various metals again shows the lawful dependence on the degree of supersaturation. The density of the vapor flow and the vapor pressure of the metal at the temperature of the collecting surface are the determining factors for the degree of supersaturation of the adsorption layer and thus for the size of the individual crystals.

Berlin, Technical University, December 1925.

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[23] Volmer and Estermann, Zeitschr. f. Physics **7**, 1 (1921).

[24] Estermann, Zeitschr. f. Elektrochemie **31**, 441 (1925), further references there.

[25] Bennewitz, Zeitschr. f. Physik. **10**, 169, (1922).